

Development of Direct Write Ink Jet for Deposition of Silver Contacts

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Abstract

Development of Direct Write Ink Jet for Deposition of Silver Contacts. LEE SMITH (University of California, Santa Cruz, 95064) Tanya Rivkin (National Renewable Energy Laboratory, Golden, CO 80401).

This project investigated the direct write printing of inks for Ag metallizations and polymer absorbers for solar cells. The basic thrust is to develop an integrated ink jet system capable of versatile printing with a variety of inks. We successfully developed a new printing system and printed Ag inks and attempted to print polymer-based inks.

Category (circle one): Material Science -- Engineering -- Computer Science

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Introduction

Motivation

An ongoing mission in the commercial photovoltaic industry is to reduce the cost of production while maintaining or increasing the efficiency of solar cells. Ink jet printing is a direct write approach to deposition of various electronic materials that has the potential to reduce the cost of solar cell processing. It may also be a critical technology for the development of next generation polymer solar cells. Since liquid precursors or inks of many of these polymers can be made, it may thus be possible to print entire solar cells with an ink jet which should reduce production cost and complexity and materials waste. In addition to being a useful tool for the development of the next generation photovoltaics, ink jet printing may also have a significant impact on conventional Si solar cell technology that at present dominates the market.

Currently, screen printing and vacuum deposition are the two major techniques used by the solar cell industry to deposit silver contacts. Vacuum deposition is capital intensive and hard to integrate in process streams. Screen printing is current standard for commercial manufacturing of many solar cells, though lower cost it has the drawbacks of low resolution, materials waste, and being a contact approach. Ink jet printing offers an alternative to both of these methods that is cheaper and could produce more efficient cells because of higher resolution and is non-contact with no additional patterning required.

Ink jets have three distinct advantages over the standard screen printing technique. First, ink jets offer the possibility of increased resolution. Screen printing is limited to about 100 micron resolution, but ink jets have the potential of increasing the resolution to less than 20 microns (Rivkin et al., 2001). Increased resolution leads to higher efficiency

cells because of less shadowing. Second, ink jet printing, is a non-contact deposition technique, which is ideal for processing thin and fragile substrates. In order to reduce the material costs and improve performance, the photovoltaic industry is tending to use thinner substrates. They are trying to go below 100 μ m for cell thickness. These thinner substrates often break under the screen printing process. Third, ink jets are a direct write technology; they only print ink where ink is desired eliminating photolithographic process and allowing flexibility on the fly. In contrast to this, screen printing requires the ink to be spread over a large screen. While some ink can be reused, a significant amount dries on the screen and is wasted. Also, as a result of the ink drying, the screens should be often cleaned and replaced, which adds to the overall cost of the process. If ink jets replaced screen printing, the overall cost of manufacturing could be significantly reduced.

Background

Modern ink jets are capable of generating small sized (less than 20 micron) drops. Liquid precursors of electronic materials can be printed with an ink jet to produce various components for medium resolution solid-state devices. There are several approaches to formulating these liquid precursors. They can be composed of dissolved organometallic compounds or polymers, colloidal suspensions of nanoparticles, or some combination of these constituents. Using organometallic inks, the desired material is formed upon thermal decomposition of the organometallic molecule which contains the atom or atoms of interest in the final materials. It is important that all of the organic constituents be volatile so that only the pure desired materials are formed. For example, a pure silver film was produced from silver(hexafluoroacetylacetonate)(1,5-cyclooctadiene) or Ag(hfa)(COD) dissolved in an organic solvent by spray deposition on a heated substrate

at a relatively low temperature (350 °C) (Rivkin et al., 2001). The addition of nanoparticles to this organometallic ink allows higher deposition rate. In this composite ink, the organometallic precursor serves as a glue that promotes the electric contact between the particles and the adhesion to the substrate, while the nanoparticles provide the bulk of the conducting material. It is important to make sure the ink formulation is compatible with the particular ink jet system chosen for deposition. When the colloidal inks are used, the particles comprising the colloid should be small and unagglomerated in order to prevent clogging of the jet. Also the liquid ink should have mechanical properties such as viscosity and surface tension within the range specified for the ink jet. Likewise, the ink jet system for deposition of various inks should be carefully chosen. For example, piezoelectric driven ink jets are more suitable for deposition of organometallic inks than thermal ink jets, where the drop is produced via formation of a bubble by locally overheating the precursor. Such overheating could cause premature decomposition of the precursor that would compromise the performance of the jet.

Goals and History of the Project

This project was started to explore the possibility of using ink jet printing to directly write circuit components and whole circuits with custom designed inks. One of the first materials was a silver organometallic ink which was suitable for printing and yielded high conductivity metal. Initially the inks were tested by spray deposition. Silver coatings were produced on silicon, glass and polymer substrates with these organometallic and composite organometallic/nanoparticle inks at 300 – 400 C. The silver was dense, pure and highly conductive (Rivkin et al., 2001). It was surprising and

encouraging that these coatings demonstrated adhesion to Silicon that was superior to that of the screen-printed films. As a second step the organometallic inks were tested with a commercial Epson ink jet printer that was modified to allow printing on a heated substrate. The silver ink our team had developed had different physical properties such as viscosity and evaporation rate from the water based inks conventionally used in Epson ink jet printers. While the printer did produce testable silver depositions, it did not allow optimization of printing conditions for our customized inks, which resulted in low resolution of the printed patterns.

To satisfy this need for use of different inks the group purchased a number of ink jet components from Microfab Inc. The Microfab ink jet is a research tool that allows a large degree of control over printing parameters. Parts of this device had been purchased by our group and partially assembled by my arrival. The objective of my work during the summer was to assist in the assembly and evolution of the complete ink jet system and develop an integrated controller to operate all of these parts. The design emphasized modularity of ink jet parts to allow printing of different inks (see Figure 3).

Materials and Methods

Ink Jet Design and Assembly

The following parts were purchased from Microfab: an ink jet print head, a print head driver, a strobe driver, and a strobe. The ink jets purchased are composed of two basic parts: a small, glass tube and piezoelectric material, partly surrounding the tube (see Figure 1). A relatively large ~1mm opening on one side of the tube is designed to provide a continuous feed of ink from the precursor cartridge. On the other side of the

tube, the internal diameter reduces to 50 microns. This end determines the size of the drops formed. When a voltage pulse is applied to the piezoelectric crystal, it contracts, generating a hydraulic transient pressure pulse or aquatic sound pulse, which ejects a drop of liquid out of the tip (Wallace & Hayes, 1987).

First, a test printer was constructed with the above parts and a used x-y-z transition stage and heater. The printer was mounted such that the jet was suspended from the x-y transition stage of the substrate heater. The jet was then moved physically in the x-y plane and was controlled by an Apple computer (see Figure 2). The z-axis was not operational and was controlled by a lab jack. A large heating plate was mounted under the X-Y stage that heated the substrate. The Microfab Jetdrive III driver interfaced between the ink jet head and a 486 laptop. When initiated by computer command, it sends a voltage pulse to the piezoelectric that triggers drop ejection (Figure 7). The advised voltage pulse shape from the manual was used. It consisted of a positive pulse of variable length and amplitude followed by a negative pulse of the same amplitude but two times the length. The ink was suspended in a syringe from a rod slightly higher than the ink head and connected via a tube to the ink jet. An analog camcorder with external lenses was used to observe the ink jet. This first generation printer was assembled as quickly as possible to test the general design before a heater and expensive high precision x-y transition stage were purchased. Hence, care was not taken to make the original printer an easy to use system. This initial testing allowed us to conclude that the movable jet approach is not optimal since the “artificial” wind produced during the motion of the head altered the conditions the jet was optimized for and caused jet instability.

The next generation ink jet system was constructed with a stationary jet and the new one micron resolution x-y transition stages that were mounted on an optical table (see Figure 3). A new custom heater was mounted on top of this stage. It was composed of an aluminum vacuum mount and insulating ceramic base (see Figure 4). This heater was attached to the transition stage and the ink jet was fixed vertically above it. A 3com HomeConnect Camera with a custom zoom lens was mounted to observe the ink jet. The strobe light illuminating the jet was positioned near the print head synchronized to the ink jet pulse. This setup allowed stop action imaging of the jet drops as in Photographs 1 and 2.

I developed a new Labview control program to control the x-y transition stage. The program works by taking the desired location and movement specifications inputted by a researcher and generates a series of machine commands, which are then written to the x-y stage through a GPIB/ IEEE interface. I chose a comb-shaped test pattern to allow the optimization of both line and solid shape printing. The comb pattern prints a series of teeth. With each tooth a major printing parameter such as the speed of x-y table, number of lines per tooth, separation between the lines, number of layers, and time delay between layers can be incremented (see Figure 6). This allows the researcher to perform combinatorial studies, which accelerates research, and can more easily show trends. The operation of this complex program is greatly simplified with a user-friendly interface, which allows the execution of customizable presets with the click of a button. In addition, each experiment is automatically logged into a file, which can be easily accessed, edited and printed in the control program. This frees the researcher from logging the many parameters by hand.

Ink preparation

A saturated solution of Ag(hfa)COD in organic alcoholic based solvent, filtered through a 0.2 μm syringe filter, was used as the organometallic Ag ink (Curtis et al., 2000). The solvents used in the study were ethanol, propanol and butanol. These alcohols have different physical properties and they were consequently tested in our printing optimization studies (Vest, 1986). The main objective of this study was to achieve stable drop generation and obtain high printing resolution.

The three factors that influence line resolution and quality are the size of the drop, the drop spreading and convection/interaction between the neighboring drops as deposited. The evaporation rate, viscosity, and surface tension of the solvent affect both the initial drop ejection and the interaction on the substrate. These combined with the properties of the hydraulic transient are theorized to influence the ejection behavior. Ideally, one wants to minimize the above mentioned properties of the solvent. This allows for smaller drop size. However, once the droplet impacts the slide, the undesirable spreading of the drop occurs if these parameters are low (Maenos, Dushkin, Saita, & Yamaguchi, 1999). Hence, the ideal solvent is some compromise of the above theological properties. Drop interaction is a more complex phenomenon and it was studied with drop evaporation experiments.

Drop Evaporation Experiments

It is difficult to observe drop formation during printing. The heater could damage the camera and the speed at which drops are dispensed by the ink jet is rather fast. To study the evaporation and interaction of drops on a hot substrate it is easier to perform a

macroscopic experiment. To do this an eyedropper was used to dispense a black writing ink mixed with ethanol at different intervals on a heated glass slide. For some of the experiments the slide was placed on a heater to observe the effects heat has on the shape of the deposition and rate of drop evaporation.

Results

The x-y transition axis controller program is fully operational containing the features listed above. The ink jet system is fully operational.

Ink Jet Experiments

Ethanol-based ink could only be printed at frequencies of 2000 Hz. Substrate temperature was around 120 °C. The best resolution achieved with the ethanol inks was 200 µm. Films did not adhere well to the substrate.

The butanol-based inks produced highly stable jets in a wide frequency range between 75 Hz and 2000 Hz. The voltage could be lowered to 20 volts at high enough frequencies when it was desired to reduce volume of the drops. At low frequencies the voltage was raised because drops became difficult to see with the camera. It was not clear whether the jet ceased operation under these voltages or simply was not visible. Below 75 Hz the jet could not be observed. The jet never became noticeably unstable at any frequency with voltages below 30 volts.

Organo-metallic ink in butanol was deposited onto a glass slide. The heater was set at 250 °C (~120 °C on the surface of the substrate). The silver depositions can be seen in Photographs 3a through d. At the deposition rate of 16 drops/mm there is no overlap of the 100-micron diameter drops and individual drops can be seen. However, at

26 drops/mm there is significant overlap. This overlap causes drop interaction that leads to redistribution of the liquid precursor on the surface of a substrate. Apparently the drops merge which upon drying results in higher diameter (up to 1mm big) round deposits connected by narrow line trace (Photograph 3b). From the microscope inspection the white-colored deposits appear to be relatively pure silver. These Ag films showed good adhesion, Scotch tape could not remove the deposits. Propanol- based inks produced stable jets only at frequencies above 700 Hz. The experiments done with propanol at 700 Hz resulted in the similar pattern of large (≈ 1 mm) drops with narrow traces between them. The speed of the jet ranged from 15 to 25 mm/s.

For all of the solvents, organometallic compound tended to deposit inside the ink jet tip after ~ 20 -30 minutes of printing. This was probably due to heating of the jet by radiation from the substrate heater. The phenomenon was not observed during the jet optimization process when the heater was not used. This decreases the performance of the ink jet and causes the ink jet to require reoptimization periodically.

Drop Evaporation Experiments

Individually deposited drops looked similar to the deposits in Photograph 3a upon drying. The size of the drop depended on the substrate temperature: higher temperatures led to smaller drops. When drops were deposited onto a room temperature slide so that they overlapped they merged into a single large drop and dried in the center of the slide with low density deposits where the drops were originally printed, (see Figure 6a). When overlapping drops were deposited onto the slide with time given to evaporate between each drop deposition, they did not seem to interact at all (Figure 6b). . Under certain drop

deposition rates and temperatures the drops began to merge but dried before they had time to fully merge leaving a relatively straight track like deposition (Figure 6c).

Discussions and Conclusion

Since ethanol could not print at adequate resolutions, butanol was used. The stability of butanol was promising but the periodic drop anomalies were not ideal (Photograph 3b and d). These were theorized to be caused by the lower evaporation rate, viscosity, and surface tension of butanol when compared to ethanol. Hence, propanol, an alcohol whose boiling point is between those of ethanol and butanol, was tried. We have not yet tested propanol enough to make conclusions about its effectiveness as a solvent. Although the tests that have been done are not promising. Frequencies of 700Hz make it difficult to move the x-y stage fast enough to prevent drops being deposited very close together. This contributes to drop spreading, drop convolution and widening of the lines. Drop evaporation experiments show that it is possible to create a continuous line-like phenomena (Figure 6c) with an eyedropper. Therefore, it is probably possible to print lines without the drop anomalies seen in Photographs 3b and d by careful adjustment of the solvent properties and heater temperature. Further work needs to be done in this area.

We have demonstrated that by printing butanol-based inks on a heated substrate it is possible to get good adhesion with good overall resolution. The temperature of the substrate and the printing speeds need to be optimized to achieve a continuous line without irregularities. In future experiments composite nanoparticle/organometallic inks will be tested and the deposition parameters for the composite inks will be optimized.

Acknowledgements

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Figure 1: A Piezoelectric Ink Jet Head

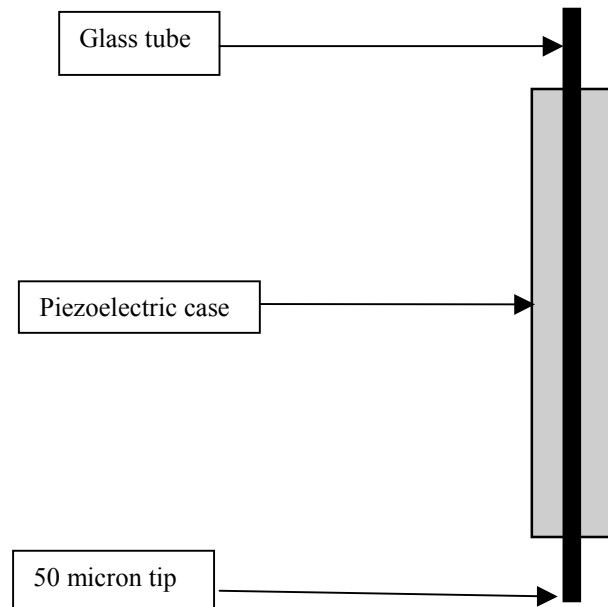


Figure 2: The Ink Jet Printer Schematic

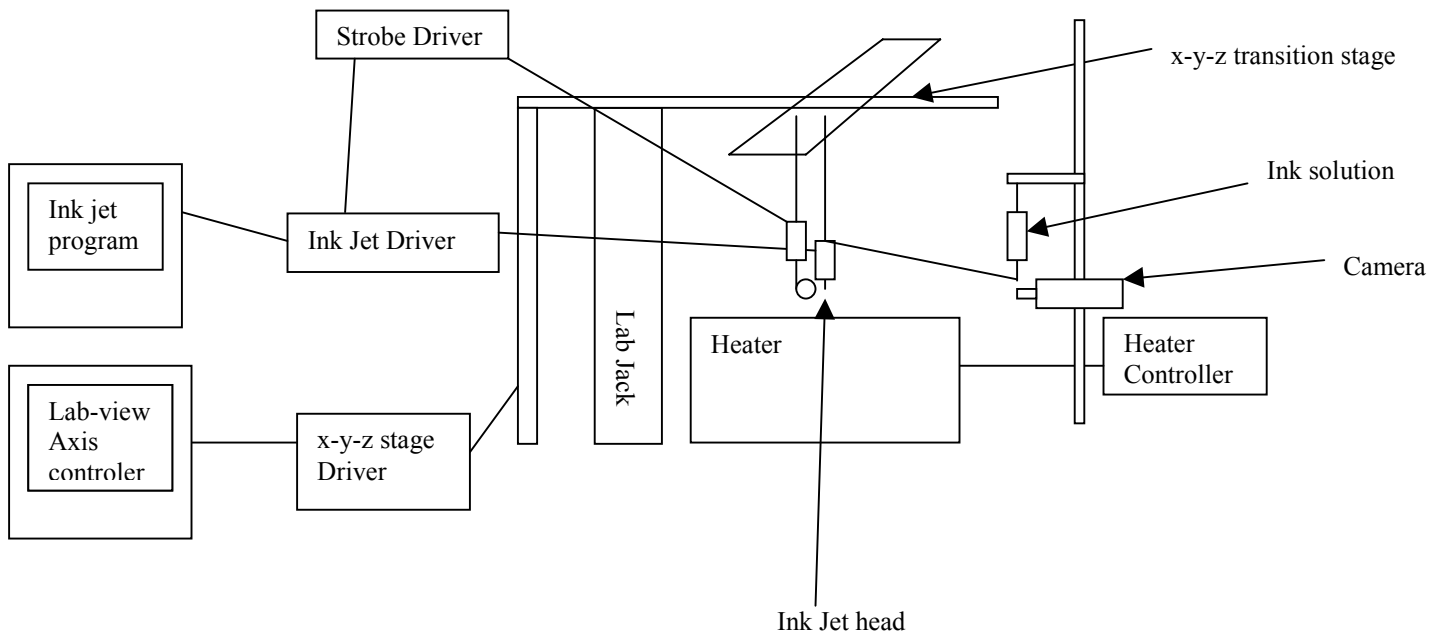


Figure 3: Desired Ink Jet Printer Schematic

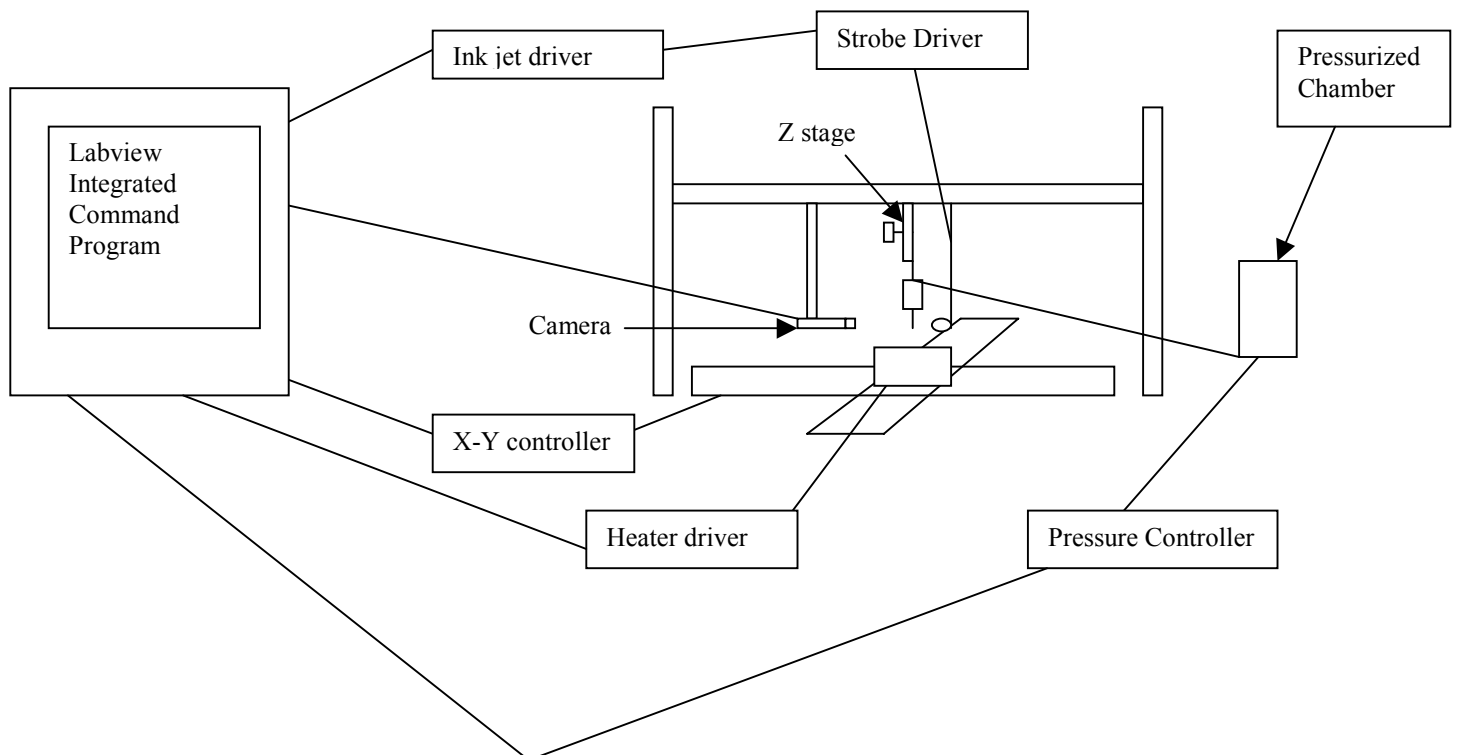
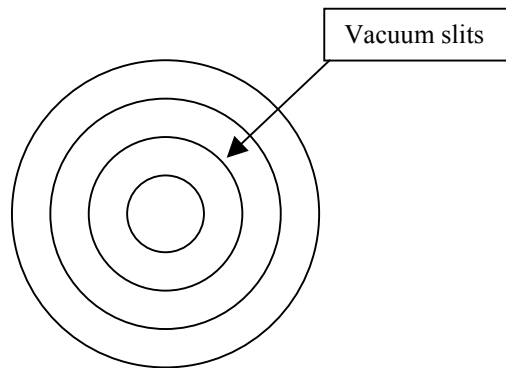


Figure 4: The custom designed heater

Top View



Side View

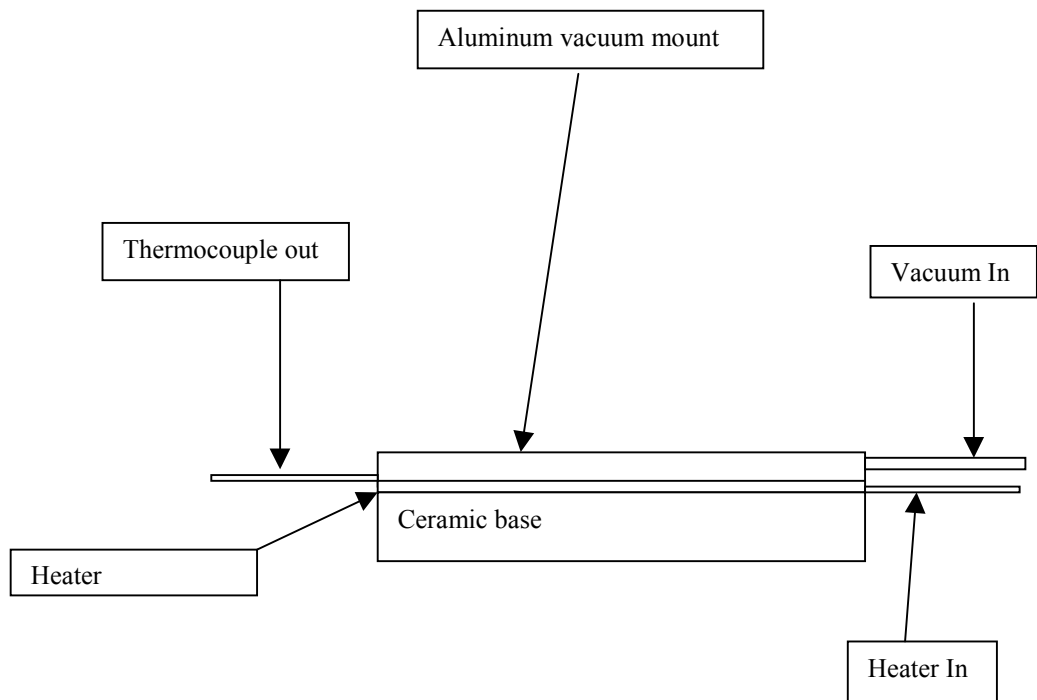
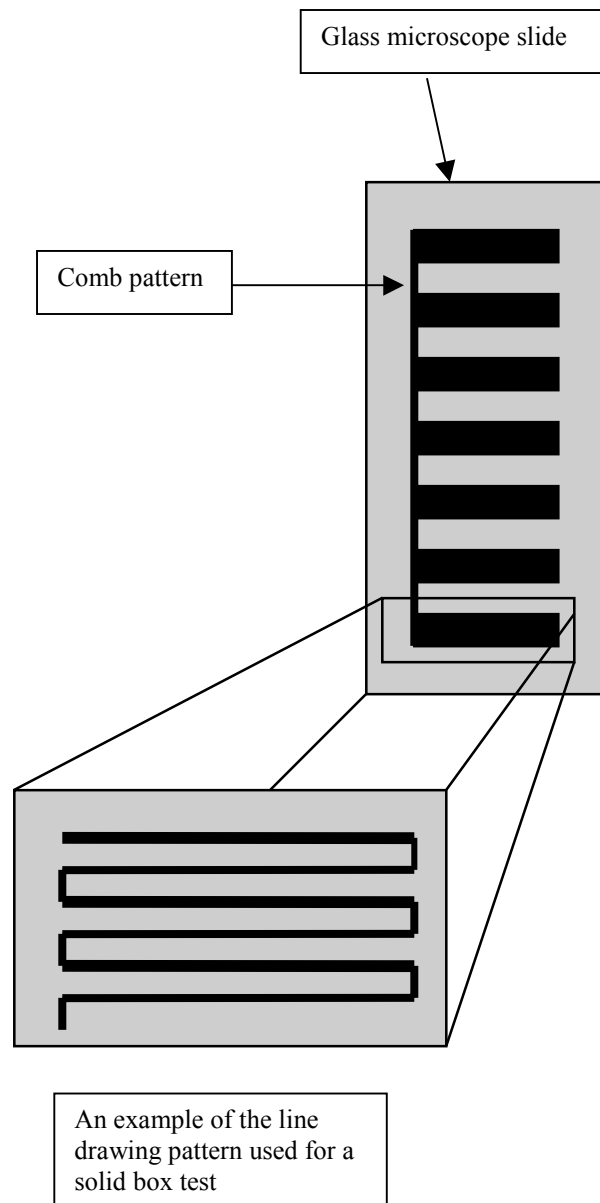


Figure 5: Slide Example



Drop Evaporation Results

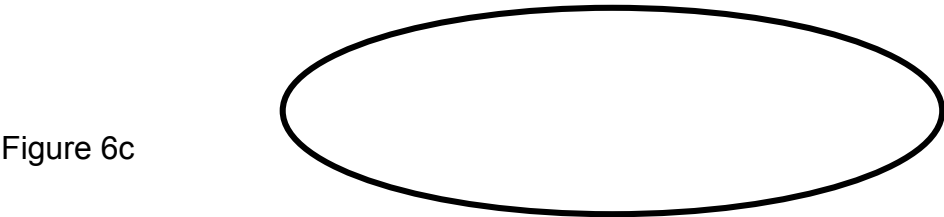
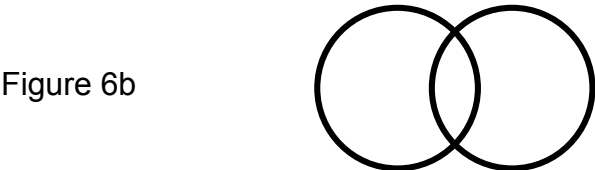
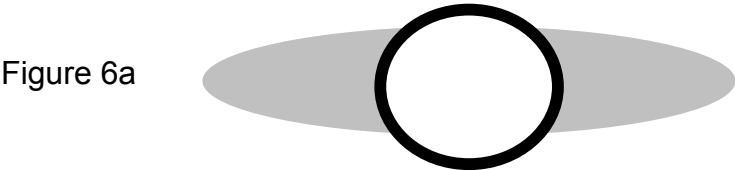
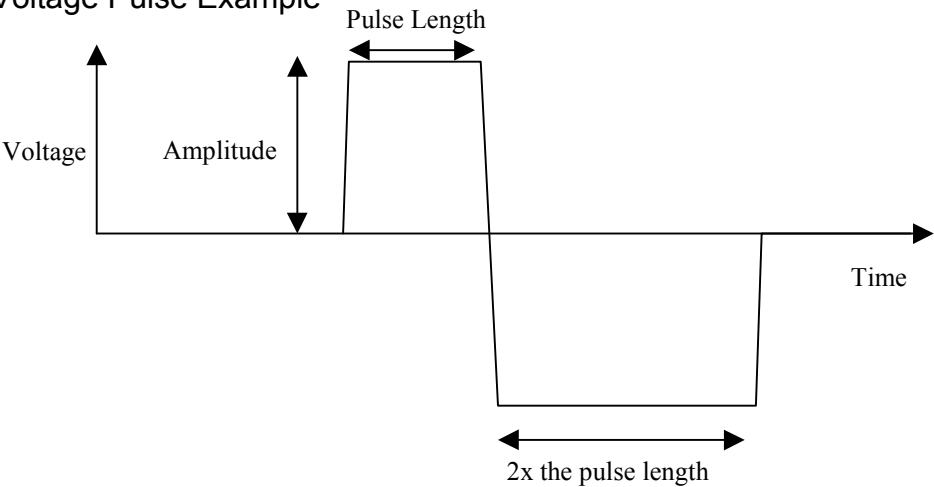
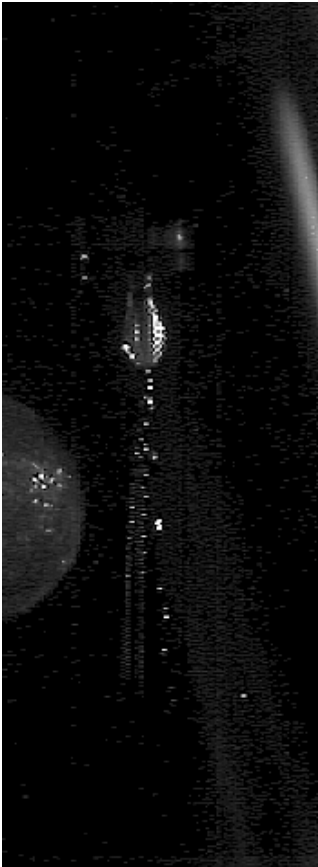


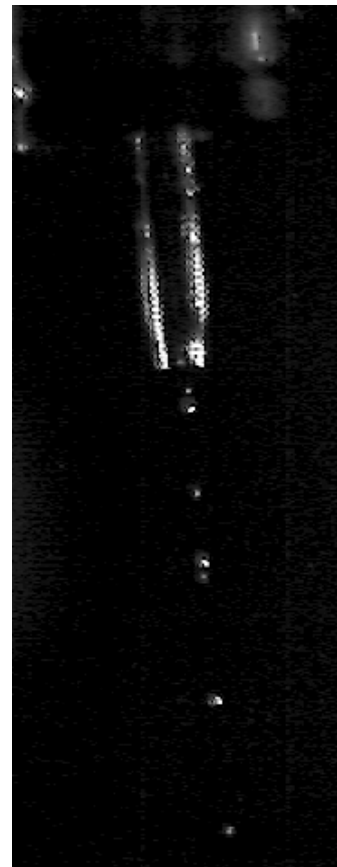
Figure 7: Voltage Pulse Example



Photographs



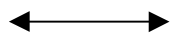
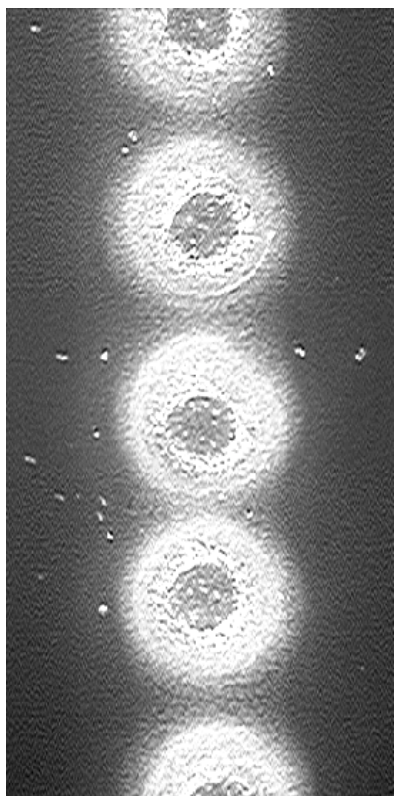
Photograph 1: A poorly optimized jet



Photograph 2: A well optimized jet

Depositions of silver ink in butanol

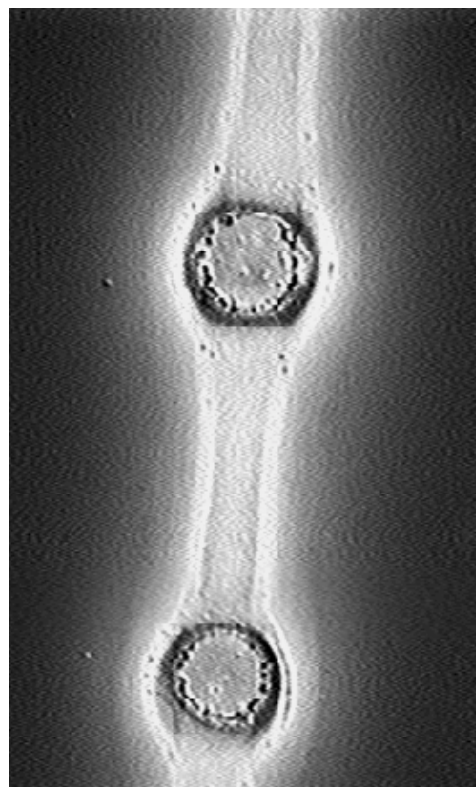
16 drops/mm



Photograph 3a

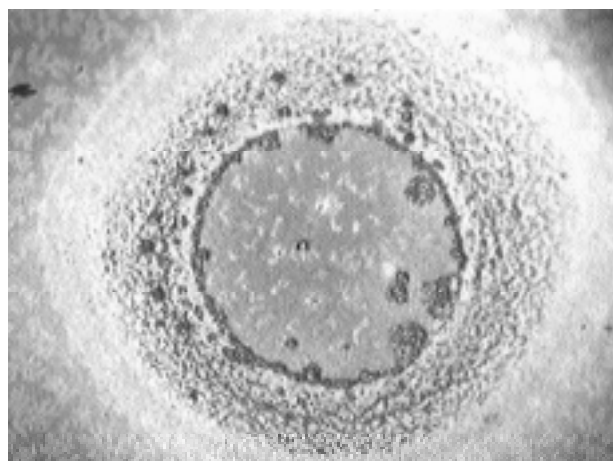
200x

26 drops/mm



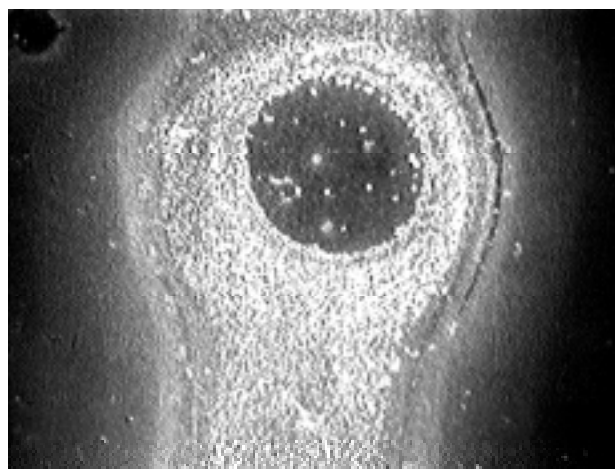
Photograph 3b

100x



Photograph 3c

500x



Photograph 3d

200x

